

Title: Development of Mesoporous Membrane Materials for CO₂ Separation

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Grant number: DE-FG2600-NT40823

Performance period: 1/1/01-12/31/01

Abstract

The emissions of carbon dioxide from fossil fuel fired power plants and industrial plants over the last century have resulted in an increase of the atmospheric carbon dioxide concentration. Climatological modeling work has predicted severe climate disruption as a result of the trapping of heat due to CO₂. As an attempt to address this global warming effect, DOE has initiated the Vision 21 concept for future power plants. In this research, we address several requirements in the Vision 21 concept by synthesizing mesoporous membrane materials that can be used to separate CO₂ from the gas effluent generated from power plants.

The current approach to separate CO₂ from other gases, especially N₂, in the hot gas effluent of power plants has been the use of zeolite membranes. Zeolites are microcrystalline aluminosilicates that have pores in the order of < 1 nm. The gas permeability of zeolites is limited due to the tortuous pore structures. In addition, the selectivity between CO₂ and N₂ by zeolites is low because the kinetic diameters of CO₂ and N₂ are similar in size. Recently, there were several studies indicated that the selective adsorption of CO₂ could be an effective way of enhancing the permeation of CO₂. The idea is to have adsorption sites on the pore wall for the CO₂ to facilitate its surface diffusion along the pore wall. Higher specific surface area would increase the adsorption of CO₂ and enhance the selectivity. The new mesoporous molecular sieves developed by researchers at Mobil in the early 90s offer an opportunity for improvement. The mesoporous molecular sieves have larger pore size than zeolites and the pore size can be varied by the size of the organic template.

The selectivity for CO₂ comes from the dopants that prefer to bond with CO₂. Horiuchi et al.¹ showed that basic metal oxides in alumina could enhance the selectivity of CO₂. The addition of alkali metal oxides such as Cs₂O and alkaline-earth oxides such as BaO were shown to increase the retention time for CO₂ than pure alumina. Furthermore, the CO₂ adsorption was found to correlate with the heat of adsorption of the basic oxides. Higher heat of adsorption correlates with better CO₂ binding. On the other hand, higher surface area is expected to improve the adsorption of CO₂ as well. Rossignol and Kappenstein² have recently shown that the addition of Ba to alumina can increase the surface area at elevated temperatures. Combining the requirements of high surface area and selective adsorption of CO₂, we chose Ba as the dopant.

Our preliminary objective is to synthesize high surface-area alumina powders which can selectively adsorb CO₂ over N₂. Alumina was synthesized by two methods. One is the precipitation method using Al(NO₃)₃. It has been shown recently by Chuah et al.³ that holding the precipitated alumina in the mother liquids at higher temperatures (digestion) can increase the surface area. Another method is the templating approach that we have developed previously.⁴

Preliminary results show that the templating method produced alumina with higher surface area after 500°C heat treatment for 4 hours. Mesoporous alumina has surface area ~380 m²/g compared to precipitated alumina with 240 m²/g. At 500°C heat treatment, it is found that the addition of Ba lowers the surface area of alumina. This is reasonable since we expect the effect of Ba on the surface area to occur near the γ - α phase transition temperature (~1100°C). It is generally believed that stabilizing dopants can delay the γ - α phase transition temperature thereby avoid the destruction of the high surface-area structure of the γ phase. However, there is an interesting difference between the Ba-doped mesoporous alumina and Ba-doped precipitated alumina. For the precipitated alumina, Ba doping results in larger pore size and pore volume. On the other hand, the addition of Ba to mesoporous alumina results in smaller pore size and pore volume. The preliminary results indicate that surface area is not the only property needs to be studied. Pore size and pore volume are also important characteristics of porous materials.

Currently we are setting up the gas chromatograph to measure the effect of Ba doping on the retention time of CO₂ and N₂ as they pass through a column of the alumina powders. We will investigate how the Ba doping and the surface area affect the CO₂ and N₂ adsorption of alumina. In future work we will incorporate the doped alumina powders with porous alumina membranes for selective permeability study.

¹ T. Horiuchi, H. Hidaka, T. Fukui, Y. Kubo, M. Horio, K. Suzuki, and T. Mori, "Effect of added basic metal oxides on CO₂ adsorption on alumina at elevated temperatures," *Appl. Catal. A*, **167**, 195-202 (1998).

² S. Rossignol and C. Kappenstein, "Effect of doping elements on the thermal stability of transition alumina," *Int. J. Inorg. Mater.*, **3**, 51-58 (2001).

³ G. K. Chuah, S. Jaenicke, and T. H. Xu, "The effect of digestion on the surface area and porosity of alumina," *Microporous & Mesoporous Mater.*, **37**, 345-353 (2000).

⁴ X. Liu, Y. Wei, D. Jin, and W.-H. Shih, "Synthesis of Mesoporous Aluminum Oxide with Aluminum Alkoxide and Tartaric Acid," *Mater. Lett.*, **42**, 143-149 (2000).